

## Models for oxygen steelmaking process: theoretical analysis versus practical trends

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The theoretical and practical considerations needed for modeling of oxygen steelmaking processes are discussed. In the past, the kinetics of reactions as affected by mixing energy were emphasized to model the processes. As an improvement, the “Beta supersonic blow control” model based on kinetics, mixing energy, and also control of chaos was developed and successfully used on the shop floor. **In the present work, it is shown that that the oxygen steel making processes can also be modeled through free energy minimization approach, provided the changes on account of mixing energy are suitably incorporated. The Gibb’s energy minimization technique is explained and the model results are compared with FactSage calculations.** The contribution of droplets to decarburization reactions is estimated.

Key words: Oxygen Steelmaking, BOF and OBM, Gibb’s energy minimization, Dynamic Control, FactSage

### Introduction: what considerations must apply for modeling an oxygen steelmaking system?

The total energy in an oxygen steelmaking system is, essentially, the sum of chemical energy (resulting in the chemical potential of different elements) and the mechanical (kinetic energy) introduced by virtue of the impinging jet resulting in the motion of the metal, slag and gas phases. The driving force for minimization of chemical energy (in presence of the oxygen supplied by the jet) is the difference in chemical potential of different elements in bulk metal vis a vis the chemical potential of the elements at the site of reaction (jet, slag-metal interface, bubble- metal interface). If there is no additional mechanical energy available from the impinging jet then the reacting elements would diffuse (atomic or molecular diffusion), aided by natural convection, to the various sites and react there to change their chemical potential in the direction of equilibrium. The difference between top blowing (BOF) and bottom blowing is in the manner in which the oxygen is supplied. In both cases the chemical energy and the mechanical energy help the system to move in the direction of equilibrium as soon as some oxygen is added by external means.

In the case of bottom blowing (OBM) process the mechanical energy component is created due to the rising (predominantly CO) gas bubbles.

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Both BOF and OBM processes are almost similar in the rates of reactions except for the small differences in the chemical composition of gas and slag. In the BOF process, droplets are generated due to the action of the jet where as in the OBM process, a slag-metal-gas emulsion forms at the interface of metal and slag. The question, ‘what is the extent of contribution of droplets in BOF and of the slag -metal emulsion in the OBM’, is still unanswered. In both the processes, in the middle blow period, the FeO is added to the slag but the percentage of FeO in slag remains at a low value (usually less than 10% FeO) because of increase in slag weight due to dissolution of lime. From mass balance it can be shown that the FeO in slag is contributing little to decarburization compared to the decarburization from the oxygen jet. It means that the emulsion in OBM is not contributing a great deal to decarburization. In the case of BOF also decarburization progresses easily even in the absence of slag, for example in the case of ‘slag less refining’ practices used in Japanese steel plants. When the slag in the main blow period becomes solid due to reduction of FeO in slag even then the decarburization rate is not affected much; initially, there is only a slight increase in the decarburization rate because of the reduction of FeO in slag. In fact, that is how an operator judges that the slag is becoming ‘dry’ or ‘solid’ and he soon raises the lance to melt the slag. In the case of on-line dynamic control model the advice to raise or lower the lance is provided on-line by the model [1]. The sound meter (used in some plants) also

indicates the drying up of slag when the noise level from converter increases.

One distinct difference between BOF and OBM is the high temperature in the jet impact region in the case of BOF in which the vaporization and subsequent oxidation of iron leads to iron loss in dust (fume loss). The iron loss in dust in the early stages of the blow in BOF can be as high as 25-30 kg/ton of hot metal. The loss of iron in dust in the case of OBM is much less.

The equilibrium mass % of oxygen, from Fe-O phase diagram, in iron at temperatures around 2200 C in the jet impact region can be as high as 22%[O] when we consider iron + liquid oxide, and more than 30%[O] when we consider liquid oxide plus oxygen. Thus the solubility limit of oxygen in the region where it is delivered to metal is quite large, both in OBM and BOF. This is one reason why the thermodynamic limit of dissolution of oxygen in the simultaneous presence of FeO and iron, both in BOF and OBM, is not an issue. When carbon is present in metal, then in both the processes the decarburization rate is actually controlled by the supply rate of oxygen, implying instantaneous reduction of the FeO formed (perhaps as an intermediate product) and zero order reaction for oxidation of carbon. Some researchers have also hinted at the Marangoni effect coming into play in the case of FeO.

In some research papers on BOF, in the early blow period, the focus has been on modifying the mass transfer coefficients of elements due to the action of jet and still consider the whole reacting system as a mixed mass transport control system ( or first order reaction), with the assumption of thermodynamic equilibrium at the interface of phases. In some papers even first order chemical reaction was assumed. To tune the process control models, so as to match the predicted rates with observed values for the case of an actual BOF, not only the mass transfer coefficient but also the area and volume of reaction were dynamically adjusted depending upon the observed rates of reactions. As regards the middle blow period, the decarburization reaction in BOF and in OBM is a “zero order” reaction, implying that rate of decarburization is directly dependent on the supply rate of oxygen.

In the development of model suitable for an actual process, the aspects of chaos have also to be considered. The tuning of a dynamic control model to an actual process requires continuous monitoring of waste gas analysis, waste gas flow, waste gas temperature and pressure (hence post combustion), lance condition and position, oxygen flow rate adjustment, and also advice of additions of ore and lime. The dynamic deviations of individual parameters from the path predicted by the model are evaluated on-line and the error is characterized either as random error or due to migration of the

process into a chaotic regime. At the onset of chaos, the chaotic attractors are manipulated for modifying the control path of the process. This scheme, of incorporating chaos module into the dynamic control model, works successfully and has been implemented at a steel plant in India as “Beta Supersonic Blow Control” [1].

The BOF and OBM are turbulent systems from the view point of the large amount of mechanical (or kinetic) energy available within the system. In the initial stages of blow (up to 25% of blow time, depending upon the silicon content of metal), the degree of turbulence and its spatial distribution directs the partitioning of the chemical potential of oxygen into the reacting elements, Fe, C, Si, Mn, P, etc. We observe high FeO content in slag at the start of the blow, both in BOF and OBM. If the elements Fe, C, Si, Mn, P, are freely available in gaseous form along with oxygen, then mixing is not a problem and the whole system can be treated as a flame combustion system which minimizes its free energy, depending upon the amount of oxygen supplied at each instant for the combustion purposes. The modeling of BOF and OBM can then be done purely on the basis of free energy minimization routines.

It is well established that towards the end of blow, the oxidation rate of carbon is controlled by mass transport of carbon. In the beginning of the blow also mixing is inadequate. The BOF and OBM can therefore be treated as ‘partially mixed systems’ in the beginning of blow and towards the end of blow. The extent of this partial mixing is a function of oxygen supply rate, gas evolution rate, lance height, nozzle design, slag amount, etc. In the middle period of the blow both BOF and OBM approach the behavior of fully mixed systems because reaction order (for oxidation of carbon) is nearly of zero order. The concepts of free energy minimization can therefore be tried to model the BOF and OBM in the middle blow period. In case we want to extend the free energy minimization to model the initial and end stage of blowing, then the procedure of free energy minimization must be modified to take care of the effects of ‘partial mixing’.

In this paper, the results of application of model based on free energy minimization shall be presented first for a fully mixed system, and then for a partially mixed system, with view to compare the trend of results seen in an actual system.

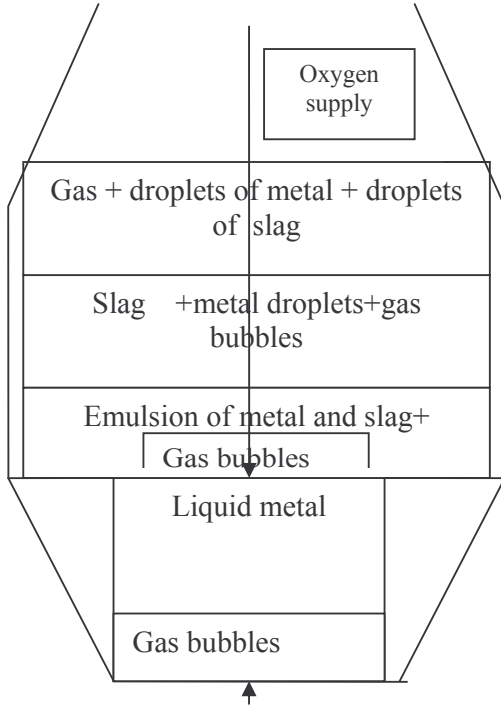
## **1. Representation of BOF and OBM as fully mixed free energy minimization system**

The requirements of a fully mixed system must be understood clearly. In a fully mixed system, the

interfaces between metal, slag and gas are assumed to be transparent. In an actual BOF or OBM, both serial and parallel paths of reactions exist, Fig. 1, in which gas can react with metal, gas can react with slag and metal can react with slag. The plant data show that in the middle blow period CO and CO<sub>2</sub> gases finally escaping the BOF are almost in thermodynamic equilibrium with the average FeO content of the slag. The slag may not be single phase at all times, and may contain di-calcium silicate, calcium ferrite, liquid iron silicate slag (containing dissolved CaO, MnO, P<sub>2</sub>O<sub>5</sub>, etc). So the idealization of BOF and OBM as a perfectly mixed system has some inherent limitations. Free energy minimization calculations will only show what is feasible in the extreme situation of infinite turbulence (i.e. when, all phases are thoroughly mixed, for example in gaseous state).

Let the metal phase contain [C], [Si],[P] and [O] in dissolved state. The slag phase contains CaO, FeO, SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. The gas phase contains CO,CO<sub>2</sub> and O<sub>2</sub>.

Fig. 1 Sequence of reactions in an oxygen steelmaking system



The total Gibbs free energy of the system is

$$\begin{aligned}
 G = & n_C \cdot \overline{G}_C + n_{Si} \cdot \overline{G}_{Si} \\
 & + n_{Fe} \cdot \overline{G}_{Fe} + n_P \cdot \overline{G}_P + n_O \cdot \overline{G}_O \\
 & + n_{SiO_2} \cdot \overline{G}_{SiO_2} + n_{FeO} \cdot \overline{G}_{FeO} \\
 & + n_{P_2O_5} \cdot \overline{G}_{P_2O_5} + n_{CaO} \cdot \overline{G}_{CaO} \\
 & + n_{CO_2} \cdot \overline{G}_{CO_2} + n_{O_2} \cdot \overline{G}_{O_2} \\
 & + n_{CO} \cdot \overline{G}_{CO}
 \end{aligned} \quad (1)$$

where  $n_i$  are number of moles and  $\overline{G}_i$  is the partial molar free energy of the  $i_{th}$  component. The conservation equations of all components yield following equality constraints:

$$n_C + n_{CO} + n_{CO_2} = A \quad (2)$$

$$n_{Si} + n_{SiO_2} = B \quad (3)$$

$$n_{Fe} + n_{FeO} = C \quad (4)$$

$$n_P + 2 \cdot n_{P_2O_5} = D \quad (5)$$

$$n_{CaO} = E \quad (6)$$

Where A,B,C,D and E are, respectively, the initial total moles of C,Si,Fe,P and CaO. The oxygen balance gives the following equation:

$$\begin{aligned}
 \frac{n_{CO}}{2} + n_{CO_2} + n_{SiO_2} + \frac{n_{FeO}}{2} + \\
 \frac{5 \cdot n_{P_2O_5}}{2} + \frac{n_O}{2} = N_{OXY}
 \end{aligned} \quad (7)$$

Where  $N_{OXY}$  is the total oxygen supplied.

In a fully mixed system, the equation (1) has to be minimized subject to the constraints (2) – (7). Let a function  $G'$  be defined such that all the equality constraints are added to equation (1) by using Lagrange multipliers:

$$\begin{aligned}
 G' = & n_C \cdot \overline{G}_C + n_{Si} \cdot \overline{G}_{Si} + n_{Fe} \cdot \overline{G}_{Fe} + n_P \cdot \overline{G}_P + n_O \cdot \overline{G}_O \\
 & + n_{SiO_2} \cdot \overline{G}_{SiO_2} + n_{FeO} \cdot \overline{G}_{FeO} \\
 & + n_{P_2O_5} \cdot \overline{G}_{P_2O_5} + n_{CaO} \cdot \overline{G}_{CaO} \\
 & + n_{CO_2} \cdot \overline{G}_{CO_2} + n_{O_2} \cdot \overline{G}_{O_2} + n_{CO} \cdot \overline{G}_{CO} \\
 & + \lambda_1 \cdot (n_C + n_{CO} + n_{CO_2} - A) \\
 & + \lambda_2 \cdot (n_{Si} + n_{SiO_2} - B) \\
 & + \lambda_3 \cdot (n_{Fe} + n_{FeO} - C) \\
 & + \lambda_4 \cdot (n_P + 2 \cdot n_{P_2O_5} - D) \\
 & + \lambda_5 \cdot (n_{CaO} - E) \\
 & + \lambda_6 \cdot \left( \frac{n_{CO}}{2} + n_{CO_2} + n_{SiO_2} \right. \\
 & \quad \left. + \frac{n_{FeO}}{2} + \frac{5 \cdot n_{P_2O_5}}{2} + \frac{n_O}{2} - N_{OXY} \right)
 \end{aligned} \quad (8)$$

In order to have minima for G, the following conditions should be satisfied:

$$\frac{\partial G'}{\partial n_i} = 0, \quad \frac{\partial G'}{\partial \lambda_i} = 0$$

This, in turn, results in the following equations:

$$\overline{G}_C + \lambda_1 = 0 \quad (9)$$

$$\overline{G}_{Si} + \lambda_2 = 0 \quad (10)$$

$$\overline{G}_{Fe} + \lambda_3 = 0 \quad (11)$$

$$\overline{G}_P + \lambda_4 = 0 \quad (12)$$

$$\overline{G}_{CaO} + \lambda_5 = 0 \quad (13)$$

$$\overline{G}_{SiO_2} + \lambda_2 + \lambda_6 = 0 \quad (14)$$

$$\overline{G}_{FeO} + \lambda_3 + \frac{\lambda_6}{2} = 0 \quad (15)$$

$$\overline{G}_{P_2O_5} + 2\lambda_4 + \frac{5\lambda_6}{2} = 0 \quad (16)$$

$$\overline{G}_{CO} + \lambda_1 + \frac{\lambda_6}{2} = 0 \quad (17)$$

$$\overline{G}_{CO_2} + \lambda_1 + \lambda_6 = 0 \quad (18)$$

$$\overline{G}_O + \frac{\lambda_6}{2} = 0 \quad (19)$$

Equations (9) to (14) give:

$$\lambda_1 = -\overline{G}_C; \lambda_2 = -\overline{G}_{Si};$$

$$\lambda_3 = -\overline{G}_{Fe}; \lambda_4 = -\overline{G}_P;$$

$$\lambda_5 = -\overline{G}_{CaO}; \lambda_6 = \overline{G}_{Si} - \overline{G}_{SiO_2}$$

Plugging above values in Equations (15)-(19),

$$\overline{G}_{FeO} - \overline{G}_{Fe} + \frac{1}{2}(\overline{G}_{Si} - \overline{G}_{SiO_2}) = 0 \quad (20)$$

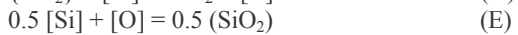
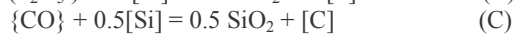
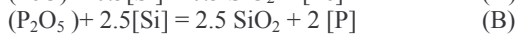
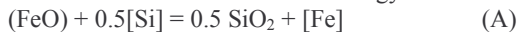
$$\overline{G}_{P_2O_5} - 2\overline{G}_P + \frac{5}{2}(\overline{G}_{Si} - \overline{G}_{SiO_2}) = 0 \quad (21)$$

$$\overline{G}_{CO} - \overline{G}_C + \frac{1}{2}(\overline{G}_{Si} - \overline{G}_{SiO_2}) = 0 \quad (22)$$

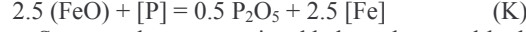
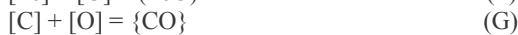
$$\overline{G}_{CO_2} - \overline{G}_C + (\overline{G}_{Si} - \overline{G}_{SiO_2}) = 0 \quad (23)$$

$$\overline{G}_O + \frac{1}{2}(\overline{G}_{Si} - \overline{G}_{SiO_2}) = 0 \quad (24)$$

Equations (20)-(24) imply that  $\Delta G \rightarrow 0$  for the following chemical reactions while the system marches towards minimum free energy:



The following reactions are also possible:



Suppose that oxygen is added to the metal bath. The free energy of reactions (E),(F) and (G) before supplying oxygen is given as:

$$\Delta G_{Si} = \Delta G_{Si}^o +$$

$$RT \ln \left( \frac{(\gamma_{SiO_2} \cdot X_{SiO_2})^{0.5}}{(f_{Si} \cdot [Si])^{0.5} \cdot f_o \cdot [O]_{eq}} \right) = 0 \quad (25)$$

After supply of oxygen the free energy of reaction (E) becomes:

$$\Delta G_{Si} = \Delta G_{Si}^o +$$

$$RT \ln \left( \frac{(\gamma_{SiO_2} \cdot X_{SiO_2})^{0.5}}{(f_{Si} \cdot [Si])^{0.5} \cdot f_o \cdot ([O]_{eq} + \Delta[O]_{Si})} \right) \quad (26)$$

From Equations (25) and (26), the following equation is derived:

$$\frac{[\Delta O]_{Si}}{[O]_{eq}} = \exp \left( -\frac{\Delta G_{Si}}{RT} \right) - 1 \quad (27)$$

The oxygen dissolved in excess of equilibrium amount will be consumed and free energy of reaction (26) will tend towards zero.

Similarly, if we consider reactions (F) and (G),

$$\frac{[\Delta O]_{Fe}}{[O]_{eq}} = \exp \left( -\frac{\Delta G_{Fe}}{RT} \right) - 1 \quad (28)$$

$$\frac{[\Delta O]_C}{[O]_{eq}} = \exp \left( -\frac{\Delta G_C}{RT} \right) - 1 \quad (29)$$

From equations (27),(28) and (29) it turns out that supplied oxygen will distribute itself in the

$$\text{ratio of } \left( \exp \left( -\frac{\Delta G_{reac}}{RT} \right) - 1 \right)$$

$$\text{or } \left( \frac{\Delta G_{reac}}{RT} \right) \quad \text{if } \Delta G_{reac} < RT.$$

A model has been developed for free energy minimization with above equations. The Gibb's energy minimization was also done by using the FactSage model for the above conditions. It must be noted that the FactSage calculations are valid only for a fully mixed system. The results of both the approaches will be compared.

## 1.1 Results and discussion of free energy minimization

The calculations are done for a fully mixed system with the following initial conditions:

Hot metal = 150 tons, Si\_HM = 0.8%, C\_HM=4.5%, P\_HM = 0.1%, Temperature of hot

metal = 1300 C. Oxygen flow rate = 500 NM<sup>3</sup>/min, Lime dissolution rate = 1 ton/min and scrap dissolution rate = 1 ton/min.

In the model developed for a fully mixed system, different levels of oxygen super-saturation of the bath with respect to C-CO equilibrium (much less than the oxygen super-saturation given by Fe-FeO equilibrium at elevated temperatures) are assumed and the calculated results are presented in Figures 2 and 3.

Fig. 2: Decarburization rate for different levels of oxygen super saturation for case 1

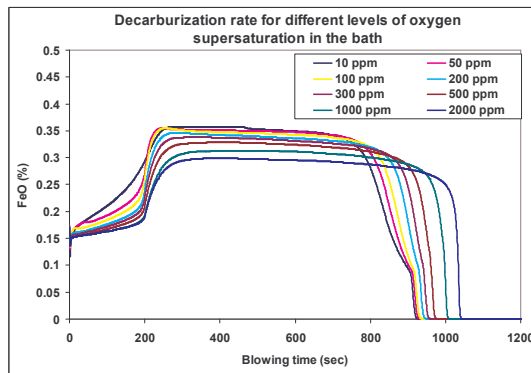
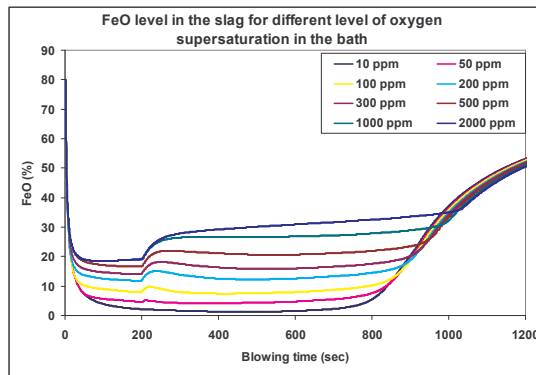


Fig. 3: FeO level in the slag for different levels of oxygen super saturation for case 1



The results obtained using Gibb's energy minimization model show a rough similarity in the trend of curves seen in practice for BOF steelmaking process, except for the initial and final part of the process, for the situation when oxygen over saturation in the bath is of the order of 100-200 ppm. The predicted trend is even closer to the OBM process when the assumed super-saturation in the bath is of the order of 50-100 ppm (Figure 3).

The calculations were also done using FactSage 6.2 package for the similar conditions. The Equilibrium module was used for the open system where a feed equivalent to the oxygen, lime and scrap equivalent to one second is given for 1000 steps. FTOxid database was used for slag solution, FTmisc was used for liquid metal and Fact53 was

used for gaseous phase. The results of calculations using FactSage are shown in Figures 4-9.

Fig. 4: Decarburization rate vs time as calculated by FactSage 6.2

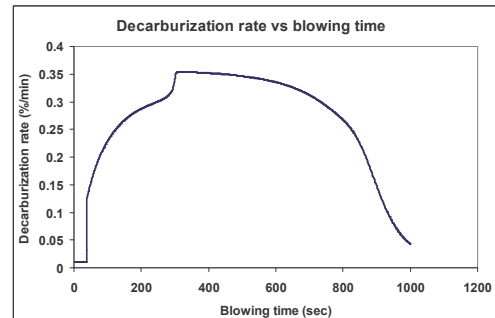


Fig. 5: FeO vs time as calculated by FactSage 6.2

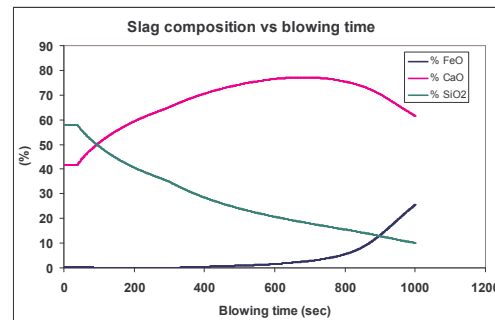
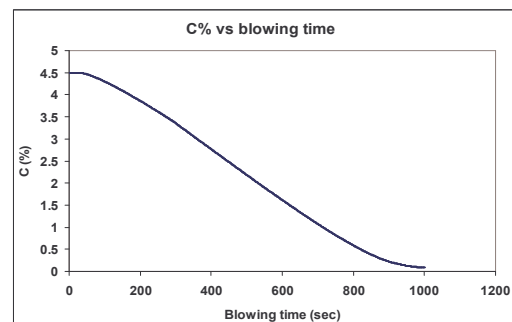


Fig. 6: C% vs time as calculated by FactSage 6.2



It can be seen from FactSage calculated results that the trend of decarburization rate predicted by FactSage is in agreement with the trend seen in that actual process in the middle blow period (Figure 4). The FactSage results show a trend similar to those calculated by Gibb's energy minimization model for the fully mixed reactor (Figure 2). The main difference is that according to FactSage the FeO level is estimated to be almost negligible in the initial part and it starts building up only in the later part of the process (Figure 5).

Fig. 7: Si% vs time as calculated by FactSage 6.2

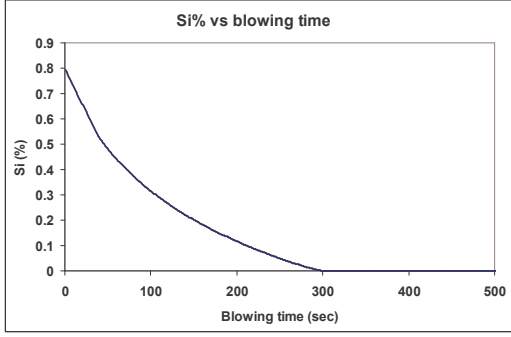


Fig. 8: P% vs time as calculated by FactSage 6.2

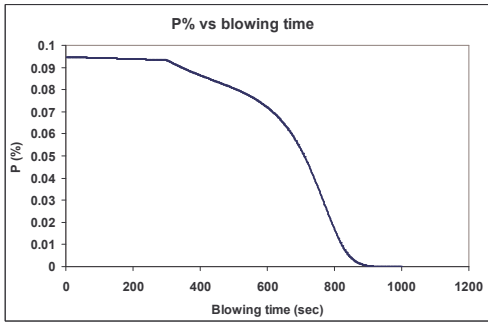
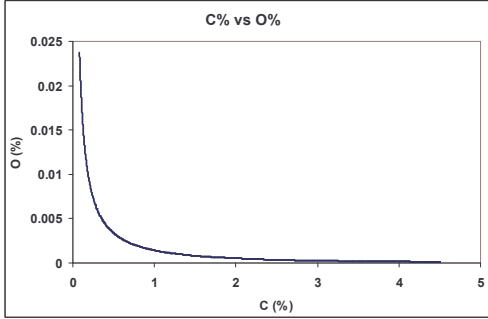


Fig. 9: %C vs %O as calculated by FactSage 6.2



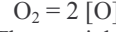
If no super-saturation of oxygen is assumed, then the results calculated by Gibb's energy minimization model for the fully mixed reactor are similar to that from FactSage (Figure 3 vs, Figure 5). The trend of silicon removal is similar to that observed in actual process (Figure 7). The dissolved carbon and oxygen level of the bath follow the equilibrium path with respect to C-CO reaction (Figure 9). Phosphorus removal rate picks up as soon as FeO is formed and it is much faster than the practical observations (Figure 8).

In the Gibb's energy minimization model for the fully mixed reactor and also the FactSage verified results, the dephosphorization and FeO in slag show deviation from the trend seen in an actual process. Phosphorus transfer is actually dependent upon slag formation (lime dissolution) which is far from

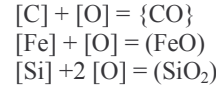
equilibrium in the major part of the blow. So far, we have not invoked the presence (or contribution) of droplets to explain decarburization occurring in the main blow period. Droplets are assumed to be same as bulk metal.

## 2. Representation of BOF and OBM as a partially mixed free energy minimization system

The oxygen supplied (from top or bottom) dissolves in metal bath,



The spatial distribution of oxygen will depend upon the distribution of mixing energy in the system. It will be spatially uniform in a fully mixed system. The dissolved oxygen reacts with the dissolved impurities and forms the respective oxides:



At a given site, it can be assumed that the dissolved oxygen is distributed between the impurities present in the iron melt in the ratio of the free energies of the corresponding reactions. This assumption, made a priori, facilitates the application of free energy minimization routine.

$$\Delta GC1 = \Delta GC1^o + RT \cdot \ln \left[ \frac{PCO}{a_C \cdot a_O} \right] \quad (30)$$

$$\Delta GFe1 = \Delta GFe1^o + RT \cdot \ln \left[ \frac{a_{FeO}}{a_O} \right] \quad (31)$$

$$\Delta GSi1 = \Delta GSi1^o + RT \cdot \ln \left[ \frac{a_{SiO2}}{a_{Si} \cdot a_O^2} \right] \quad (32)$$

$$x_{C1} = \frac{\Delta GC1}{\Delta GC1 + \Delta GFe1 + \frac{1}{2} \Delta GSi1} \quad (33)$$

$$x_{Si1} = \frac{\frac{1}{2} \Delta GSi1}{\Delta GC1 + \Delta GFe1 + \frac{1}{2} \Delta GSi1} \quad (34)$$

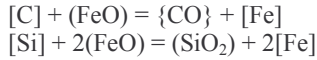
The justification for using equations 33 and 34 has already been given in Eq. 29 if we want to proceed with free energy minimization happening at each time step.

In the case of a partially mixed system, the rate equations, as also suggested in [2], are written as:

$$-\frac{d[C]}{dt} \frac{Wt\_HM}{100 \cdot M_C} = \frac{2 \cdot \eta_C \cdot FO2}{22400} \cdot x_{C1} \quad (35)$$

$$-2 \frac{d[Si]}{dt} \frac{Wt\_HM}{100 \cdot M_{Si}} = \frac{2 \cdot \eta_{Si} \cdot FO2}{22400} \cdot x_{Si1} \quad (36)$$

It is also assumed that a fraction of total iron oxide present in the slag is reduced by the following mechanisms:



The distribution of FeO between the above two reactions is in the ratio of the free energies of the corresponding reactions. The free energies are defined as [1]:

$$\Delta GC2 = \Delta GC2^o + RT \cdot \ln \frac{PCO}{a_C \cdot a_{FeO}} \quad (37)$$

$$\Delta GSi2 = \Delta GSi2^o + RT \cdot \ln \left[ \frac{a_{SiO2}}{a_{Si} \cdot a_{FeO}^2} \right] \quad (38)$$

$$x_{C2} = \frac{\Delta GC2}{\Delta GC2 + \frac{1}{2} \Delta GSi2} \quad (39)$$

$$x_{Si2} = \frac{\frac{1}{2} \Delta GSi2}{\Delta GC2 + \frac{1}{2} \Delta GSi2} \quad (40)$$

$$- \frac{d[C]}{dt} \frac{Wt\_HM}{100.M_C} = \frac{2.\eta_C.FO2}{22400} \cdot x_{C2} \quad (41)$$

$$- 2 \frac{d[Si]}{dt} \frac{Wt\_HM}{100.M_{Si}} = \frac{2.\eta_{Si}.FO2}{22400} \cdot x_{Si2} \quad (42)$$

The efficiency factors ( $\eta_C, \eta_{Si}$ ) are dependent upon concentration and the degree of mixing of the system. For the case of a fully mixed system, these factors can be assumed to be unity. In a partially mixed system their value is made to increase from 0 to 1; the value of 1 is used when silicon oxidation is over. As per the program, a sudden increase in decarburization occurs as soon as silicon oxidation is over. In the initial part of the blow in BOF and OBM, mixing of metal gradually increases as the decarburization rate increases. Therefore, efficiency factors ( $\eta_C, \eta_{Si}$ ) are assumed to vary as a function of total mixing energy of the bath as follows:

$$efficiency\ factor(\eta_C, \eta_{Si}) \propto (E_{total}^o)^n \quad (43)$$

For the sake of tuning, the efficiency parameters  $\eta_C$  and  $\eta_{Si}$  are assigned appropriate values to match model predicted values with the actual process [3], in the previous work.

## 2.1 Predictions for a partially mixed reactor

The results in the previous section show FeO should not form in initial stages of blow in a fully mixed reactor. But mixing is a real problem to tackle in the initial stages of the blow even when the droplets are present. This is because the lance is kept in high position at the start of the blow, the

metal contains un-dissolved scrap, and also a lot of lime, dolomite and ore are dumped on top of metal. Thus, owing to mixing limitations the FeO is formed in initial stages but it is reduced later on when mixing of the system increases due to lower lance height, increased decarburization and continuous scrap dissolution.

In BOF process since a lot of metal droplets are thrown into the atmosphere, we assume that these droplets are nothing but a part of parent bulk metal at each time step of blow. It may be argued that since the droplets are being produced from jet impact region which is at substantially higher temperature, the possible level of super-saturation of dissolved oxygen in these droplets is much higher. Further, FeO in bulk slag can remove carbon from the droplet. Perhaps for these reasons the carbon content of metal droplets is found to be slightly less than the bath carbon content [4].

Results are plotted for different values of oxygen super saturation in the bath, Figures 10-12. The trend of these results is in rough agreement with the trend of FeO content seen in actual process when the assumed super saturation is over 200 ppm (Figure 10), or when the FeO level in the slag is beyond 8% during middle blow period. The contribution of indirect reaction due to droplets for decarburization is estimated in the range of 10 to 25% during middle blow period and the highest contribution reaches by 30% by the end of the blow (Figure 11). The decarburization rate for assumed super-saturation of 2000 ppm (when oxygen level is in equilibrium with almost pure FeO at around 1873 K) along with the contribution from direct and indirect reaction is plotted in Figure 12. This is the case when highest possible contribution of indirect reaction (by droplets) may be observed.

Incorporation of concept of chaos into the free energy minimization model will, however, pose some fundamental issues because we cannot discuss equilibrium and chaos on the same platform.

## Conclusions

A fundamental study of oxygen steelmaking process based upon Gibb's energy minimization technique, using the models developed at IITK and also through FactSage, has been done for the case of a fully mixed reactor. It is interesting to note that that the trend of results of free energy minimization are similar to an actual process in the middle blow period, implying that both BOF and OBM processes are close to equilibrium during the middle part of blow. The difference of results between the model (based on Gibb's energy minimization technique) and the actual process for the fully mixed reactor can be attributed to lack of mixing and the gradual change in extent of mixing with time in the initial and final stages of blowing.

For the case of BOF process, there is high FeO in initial part of the process. FeO is subsequently

reduced during middle blow period, as also shown by Gibb's energy minimization.

Fig. 10: FeO level in the slag for different levels of oxygen super saturation for partially mixed reactor

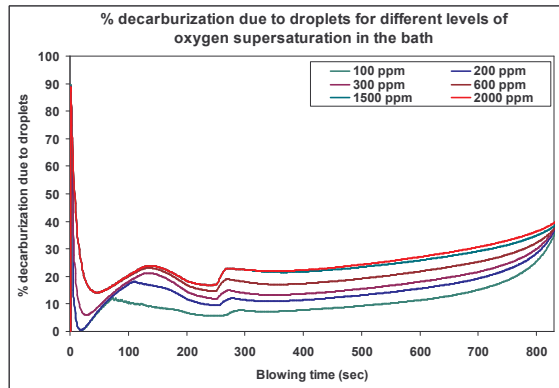


Fig. 11: Percentage decarburization due to droplets for different levels of oxygen super-saturation in the bath for partially mixed reactor

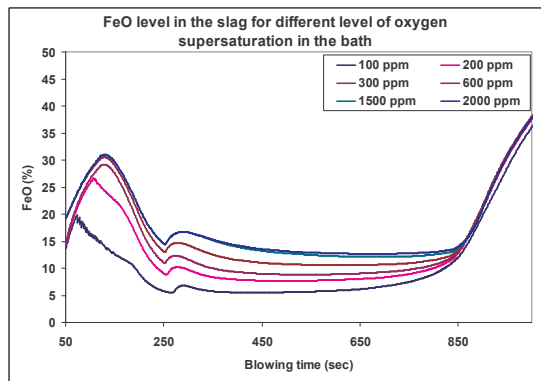
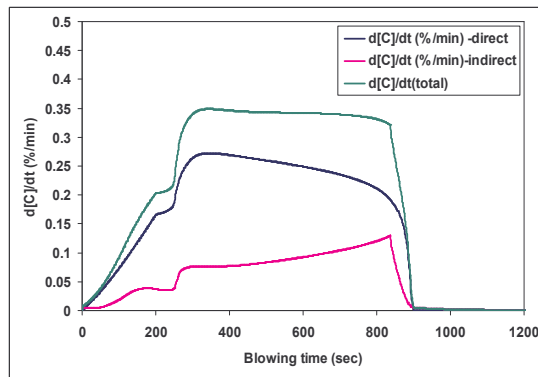


Fig. 12: Decarburization rate for oxygen super saturation as given by Fe-FeO equilibrium for partially mixed reactor



For the case of OBM process, the results, as predicted by Gibb's energy minimization technique, are in better agreement than for BOF, implying that

mixing is more efficient in the case of OBM. This is expected.

The Gibb's energy minimization model for the partially mixed reactor for BOF process predicts that the contribution of metal droplets via indirect decarburization (or through metal droplets) may of the order of 10-25% during middle blow period and approximately 30% during last part (end blow) of the process.

Dephosphorization process is not adequately explained by free energy minimization calculations. Actually, the droplets may have more important role to play in de-phosphorization, which is controlled by mass transfer in slag phase. This is because the droplets may provide extended slag-metal interfacial area for phosphorus transfer, just as they do for reducing the FeO in slag. Simultaneous processes, of FeO reduction and phosphorus transfer can occur because of greater stability of  $P_2O_5$  (vis a vis FeO), the reduced activity of  $P_2O_5$  and its capture (or physical locking) in solid di-calcium silicate ( $C_2S$ ). It is known that phosphorus reverts to metal when di-calcium silicate begins to melt because of increasing metal and slag temperature. Also the solubility of  $P_2O_5$  is highest in  $C_2S$  in oxygen steelmaking.

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